Pitch fixative selection by capillary electrophoresis

DOUGLAS S. MCLEAN[1], MICHAEL C. BREADMORE[3], KAREN R. STACK[2], DESMOND E. RICHARDSON[5], PAUL R. HADDAD[4].

SUMMARY

Wood pitch deposition has antagonised the papermaker for over two hundred years. Fixatives, chemistries which are used to attach wood resin to wood fibre, have been used to alleviate wood pitch deposition to varying degrees of success. This paper aims to present a new method by which fixatives can be evaluated at a molecular level in a short period of time.

Capillary Electrophoresis (CE) is used in many industries, including pulp and paper, as an analytical technique for the separation of analytes under the application of an electric field whereby the differences in the electrophoretic mobilities of the analytes lead to their separation. This paper makes use of CE, not for its separation of analytes but for quantification of interactions between analytes and selectivity modifiers. Electrokinetic chromatography (EKC) is a variation of CE where a selectivity modifier is included in the electrolyte. In using wood resin fixatives as selectivity modifiers and wood resin components as analytes, we were able to determine their interactions at a variety of pHs and temperatures. The result of this development is the ability to recommend a given fixative chemistry for the unique pH, temperature and extractive composition of a given pulp and/or paper mill.

Details of the methods, results and data interpretation are included in this paper.

KEYWORDS

capillary electrophoresis, wood pitch, pitch deposition, resin acids, fixatives, paper making

[1] Corresponding author; PhD Student. [2] Research Fellow.
Pulp and Paper Research Group, School of Chemistry, University of Tasmania, Private Bag 75, Hobart, Tasmania 7001.
[3] Australian Research Council Australian Postdoctoral Fellow, [4] Professor & Deputy Head of School
School of Chemistry, University of Tasmania, Private Bag 75, Hobart, Tasmania 7001.
[5] Senior Specialist Process Chemistry, Research & Development Australasia,
Norske Skog Paper Mills (Australia) Ltd, Boyer, Tasmania 7140.

INTRODUCTION

Enckell (*1*) believed that pitch deposition was due to colloidal instability and as a result theorised three possibilities by which 'rosin suspensions' (i.e. colloidal pitch) could be converted into forms that were not harmful to paper manufacture. One possibility to accomplish this was to fix the 'rosin suspension' to the pulp fibres. Wågberg and Ödberg (*2*) as well as Shetty *et al* (*3*) demonstrated that fixatives do not necessarily fix colloidal and dissolved extractives to the fibre but that fixatives simply aggregate the extractives into ~10μm sized particles. These particles are then trapped through filtration during the forming of the fibre mat on the paper machine. The term "fixative" remains the papermaking term for chemical products that help remove wood extractives from the papermaking process by way of the paper being produced on the paper machine.

Fixative chemistries have been used to control pitch deposition for nearly two hundred years. Early fixative applications of alum ($Al_2(SO_4)_3 \cdot xH_2O$) not only reduced pitch deposition (*4*) but also provided paper with sizing (hydrophobicity for improved printing) (*5*). Coagulants such as polyethyleneimine (PEI) (*6,7*), poly-dimethyldiallyl-ammonium chloride (pDADMAC) (*2*) and acrylamide co-polymers (*8*) have been effective at reducing pitch deposition.

Fixative programs are often evaluated in the laboratory by measuring the amount of pitch deposited (i.e. not 'fixed' to the fibre). Blomquist (*9*) reviewed seventeen (*10-25*) methods for the evaluation of pitch deposition most of which are also used to evaluate pitch fixatives. This paper aims to develop a new method for pitch fixative selection that is based on the interaction between wood extractives and fixatives as observed by capillary electrophoresis (CE).

Capillary electrophoresis is a free solution external electric field separation technique that was first demonstrated by Hjertén (*26*) in 1967 and then miniaturised to capillaries by Virtanen (*27*) (1974) and Mikkers *et al* (*28*) (1979). In the 1980s CE became recognised as an analytical technique mainly through work by Jorgenson and Lukacs (*29*) (1981). CE has since been used in a wide variety of analytical techniques the most notable is the sequencing of the human genome (*30*).

CE has had limited exposure in the pulp and paper industry. Useful carbohydrate (*31*) and resin acid (*32,33*) analytical techniques have been developed. Online CE (*34*) analysis of process water anions and cations looks as though it may allow the process chemist to balance complex wet-end chemistry as paper machines become more closed (i.e. use less water). The latest of these on-line techniques (*35*) can monitor cleaning, bleaching, microbial, corrosive and other chemical processes simultaneously in ~20-30 minute analytical cycles.

Electrokinetic chromatography (EKC (*36*)) is a blend of chromatography and electrophoresis which uses a pseudo-stationary phase (p-SP, selectivity modifier) in the electrolyte in order to improve the separation of analytes. In 1990 Terabe and Isemura (*37*) used a cationic polymer, pDADMAC, as their p-SP in order to improve the separation of some aromatic carboxylic acids. Nutku and Erim (*38*) used polyethlyleneimine (PEI) as their p-SP while varying the pH in order to improve the separation selectivity of their analytes. In 2000 Li *et al* (*39*) showed how varying the concentration of a p-SP and a competing ion can lead to enhanced separation selectivity. Breadmore *et al* (*40*) derived a theoretical equation to optimise the separation selectivity of a range of inorganic anions and small organic acids. From this equation, and of relevance to this paper, was the estimation of analyte p-SP interaction.

It is this quantification of the interaction (interaction factor) between the p-SP (pitch fixatives) and the analyte(s) (wood resins) through EKC that this paper is interested in exploring. This goal is far from being lofty, because of the fact that the p-SPs used in EKC are the same as the polymers used as pitch fixatives in the pulp and paper industry. The challenge is in regards to the analytes, the components that make up pitch, though they are similar to the analytes previously explored in EKC. (*38*)

EXPERIMENTAL

Analyte

The resin acid analyte was prepared as a colloidal dispersion as previously published. (*15*) The resin acid used in this study was dehydroabietic acid (DhA)(Helix-Biotech, 99% purity [1740-19-8]).

Buffers *(41,42)*

Four 20mM amine buffers, from Aldrich, were used in order to explore four specific pHs. The only amine which required additional preparation was N,O-dimethylhydroxylamine which was distilled at 100°C, with a molar excess of KOH to a yield of 82.5%, in order to obtain the free amine from the hydrochloride salt.

The pHs were obtained by titrating the amines in Table 1 with 1M HCl until the pH of the buffer equalled the pK_a of the amine. The first pH of interest was 10.93 which is above the pK_a of dehydroabietic acid (*43-46*) which ensures that the acid is ionized. The second pH explored was 8.06, a pH common to alkaline papermaking. Another pH examined was 6.85, a pH common to neutral papermaking. Finally, pH 4.75 to be studied as it is common to acid papermaking. The counter ion, or competing ion, in all four buffers was Cl^-.

Pseudo-stationary phase (p-SP, selectivity modifier)

Poly(diallyldimethyl ammonium chloride), also known as pDADMAC and PDDAC (Aldrich [26062-79-3], 20^w/o in water, molecular weight 400k-500k), was selected as the selectivity modifier.

Capillary Electrophoresis

This work made use of an Agilent ^{3D}CE instrument, Figure 3, with a Polymicro Technologies fused-silica capillary (74μm ID x 0.6m). The injection sequence is described in Table 2.

Table 1.
Physical properties Buffers

Buffer	Purity	CAS#	pK_a
diethylamine	98%	[109-89-7]	10.93
tris(hydroxymethyl)aminomethane	AR	[77-86-1]	8.06
ethylenediamine (pK_2)	99%	[107-15-3]	6.85
N,O-dimethylhydroxylamine HCl	98%	[6638-79-5]	4.75

Table 2.
CE injection sequence

Event	Pressure (mbar)	Time (s)
Flush with eluent (buffer and p-SP)	50	120
Inject analyte	20	3
(colloidal DhA ~60mg/L, with trace amounts of potassium nitrate(15))		
Rinse electrode with Milli-Q® H_2O	0	6
Inject Milli-Q® H_2O (peak narrowing)	20	0.5
Inject dilute acetone (EOF marker)	20	3
Rinse electrode with Milli-Q® H_2O	0	6
Inject eluent	20	3
(buffer and p-SP used as a plug/cap to prevent loss analyte)		

A negative polarity of 20kV was applied which resulted in currents under 100μA. Detection was by direct absorbance at 195nm (DhA^- and NO_3^-) and 254nm (electro-osmotic flow /EOF/acetone).

From the electropherograms the observed migration time of the analyte (t_{obs}) and the electro-osmotic flow (t_{EOF}) are recorded. The electrophoretic mobility of the analyte is defined as follows:

$$\mu_A = \mu_{obs} - \mu_{EOF} \quad [1]$$

$$\mu_{obs} = \frac{l \cdot L}{V \cdot t_{obs}} \quad [2]$$

$$\mu_{EOF} = \frac{l \cdot L}{V \cdot t_{EOF}} \quad [3]$$

where μ_A is the electrophoretic mobility of the solute anion (A), μ_{EOF} is the electrophoretic mobility of the electro-osmotic flow (EOF), μ_{obs} is the observed electrophoretic mobility of the solute anion (A), V is the voltage across the capillary in volts, L is the length of the capillary in metres, l is the distance, in metres, from cathodic end of the capillary to the detector.

In traditional CE, when no p-SP is added, the DhA^- migrates towards the anode and the EOF will move towards the cathode. A schematic of this is shown in Figure 4.

In EKC using a cationic p-SP (pDADMAC), the column is coated with a cationic layer comprised of the p-SP. As a result of this cationic coating the EOF moves towards the anode. The DhA^- continues to migrate towards the anode, although its migration is now impeded by, interaction with pDADMAC which migrates towards the cathode. By increasing the concentration of the pDADMAC one would expect longer migration times for the DhA^- due to more association with

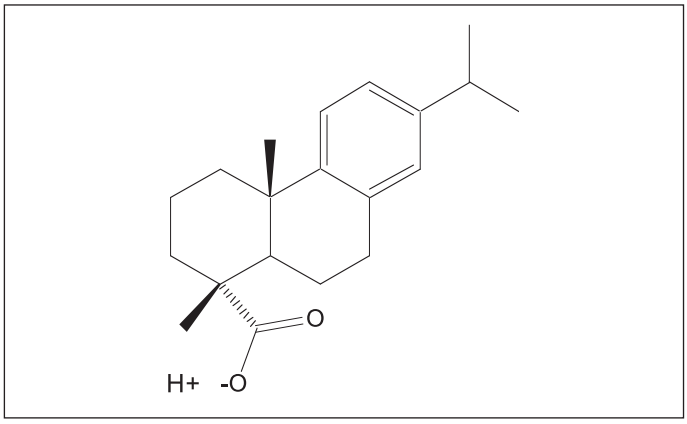

Fig. 1 Chemical structure of dehydroabietic acid.

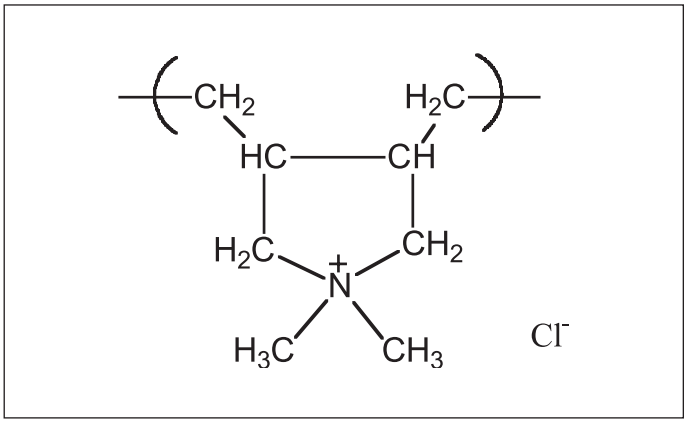

Fig. 2 Chemical structure of pDADMAC.

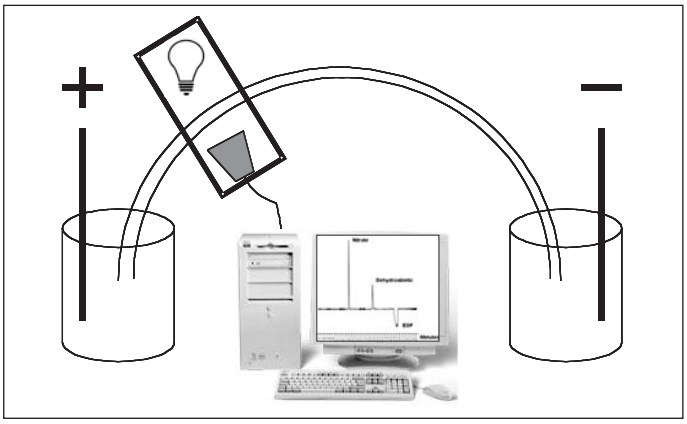

Fig. 3 Schematic of a CE instrument.

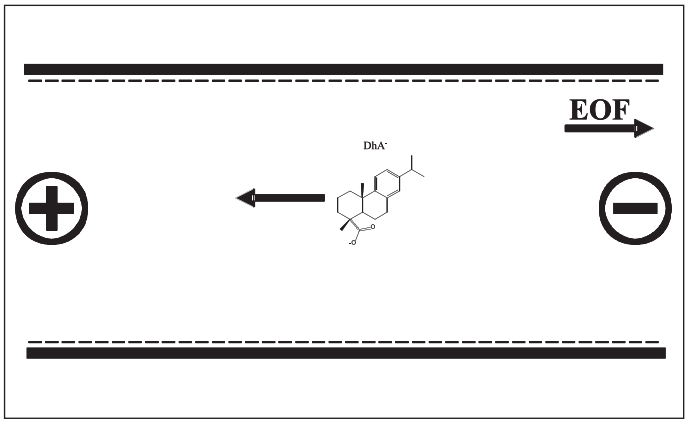

Fig. 4 Schematic of CE showing flow of DhA^-.

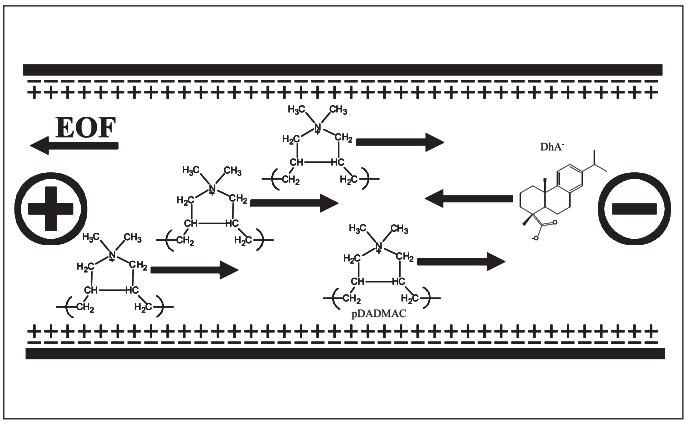

Fig. 5 Schematic of EKC showing flow of DhA^- and pDADMAC.

pDADMAC. A schematic of these EKC interactions is shown in Figure 5.

Interaction factors (*40,47*)

In an EKC system the electrophoretic mobility of the anion can be described as follows (*48,49*):

$$\mu_A = \alpha_{mp} \cdot \mu_{mp} + \alpha_{sp} \cdot \mu_{sp} \quad [4]$$

where μ_{mp} is the electrophoretic mobility of the solute anion (A) in the mobile phase, μ_{sp} is the electrophoretic mobility of the solute anion (A) in the p-SP, α_{mp} is the mole fraction of the solute anion (A) in the mobile phase, α_{sp} is the mole fraction of the solute anion (A) in the p-SP.

The mole fractions of the anion (A) in the mobile and pseudostationary phases can also be expressed in terms of retention factor, k'_A, of the solute anion (A). (*48,50*)

$$\alpha_{mp} = \frac{1}{1 + k'_A} \quad [5]$$

$$\alpha_{sp} = \frac{k'_A}{1 + k'_A} \quad [6]$$

By substituting terms from Equations 5 & 6 into Equation 4, Equation 7 is obtained.

$$\mu = \left(\frac{1}{1 + k'_A}\right) \cdot \mu_{mp} + \left(\frac{k'_A}{1 + k'_A}\right) \cdot \mu_{sp} \quad [7]$$

The retention factor, k'_A, is defined as (*51*):

$$k'_A = \left(\frac{w}{V_{mp}}\right) \cdot D \quad [8]$$

where w is the weight of the p-SP, V_{mp} is the volume of the mobile phase, D is the distribution coefficient of the analyte between the mobile and p-SP, and is further defined by Equation 9

$$D = \left(K'_{A,E}\right)^{1/y} \cdot \left(\frac{Q}{y}\right)^{x/y} \cdot [E]^{-x/y} \quad [9]$$

where x is the charge of the analyte ion. y is the charge of the eluent ion, [E] is the concentration of the competing anion (E), $K'_{A,E}$ is the selectivity coefficient of ion-exchange matrix for the solute anion (A) over the competing anion (E), Q is the ion exchange capacity of the column. (concentration of the p-SP).

By substituting Equation 9 into Equation 8, Equation 10 is obtained.

$$k'_A = \left(\frac{w}{V_{mp}}\right) \cdot \left(K'_{A,E}\right)^{1/y} \cdot \left(\frac{Q}{y}\right)^{x/y} \cdot [E]^{-x/y} \quad [10]$$

Equation 10 is simplified to Equation 11 due to the fact that the charge of the analyte ion (x), and the charge of the eluent ion (y) are –1 and +1, respectively when the pH of the eluent is above the pK_a of DhA (6.77*(45)*). If the pH of the eluent is not above the pK_a of the analyte then x and y need to be determined experimentally or theoretically.

$$k'_A = \frac{\left(\frac{w}{V_{mp}}\right) \cdot K'_{A,E} \cdot Q}{[E]} \quad [11]$$

By substituting Equation 11 into Equation 7, Equation 12 is obtained. (see next page.)

Two parameters in Equation 12 are unknown. The first unknown parameter is $K'_{A,E}$ which is the interaction factor between an ion-exchange matrix (pDADMAC) and an anion A (DhA^- in the case of this work) over a competing anion E (Cl^- in the case of this work). The second unknown parameter in Equation 12 is μ_{mp} which is the electrophoretic mobility of the solute anion (DhA^-) independent of matrix and competing anions.

The remaining parameters in Equation 12 are known. [E], Q, w and V_{mp} are all known from the concentrations by which the eluent and analytes were prepared. μ_A is the electrophoretic mobility of the anion A (DhA^- in

$$\mu_A = \left(\frac{1}{1 + \left(\frac{\left(\frac{w}{V_{mp}} \right) \cdot K'_{A,E} \cdot Q}{[E]} \right)} \right) \cdot \mu_{mp} + \left(\frac{\left(\frac{\left(\frac{w}{V_{mp}} \right) \cdot K'_{A,E} \cdot Q}{[E]} \right)}{1 + \left(\frac{\left(\frac{w}{V_{mp}} \right) \cdot K'_{A,E} \cdot Q}{[E]} \right)} \right) \cdot \mu_{sp} \qquad [12]$$

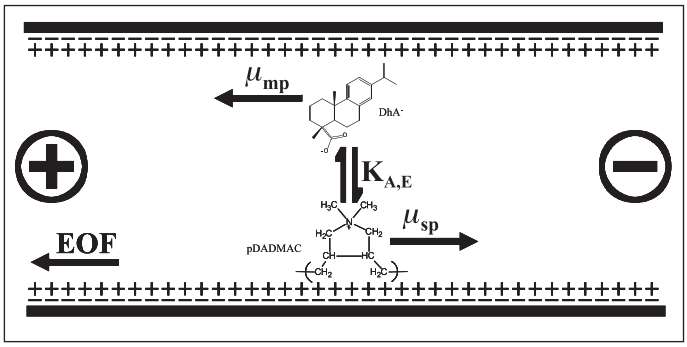

Fig. 6 Schematic of EKC interactions.

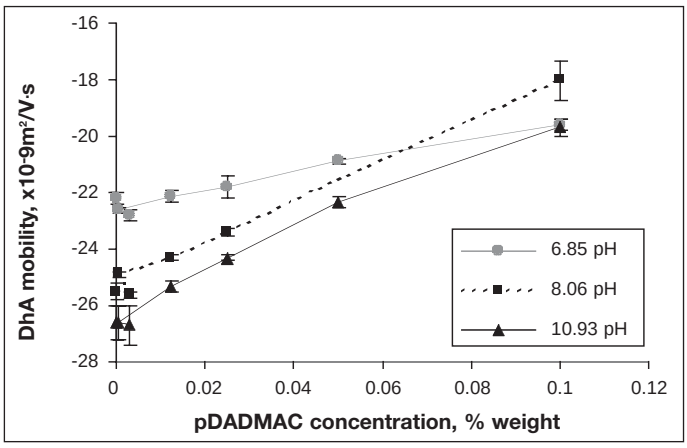

Fig. 7 pDADMAC concentration versus DhA⁻ mobility. (error bars indicate +/- 1 std. dev.)

Table 3.
DhA/pDADMAC interaction factors and DhA mobile phase mobilities.

pH	6.85	8.06	10.93
$K'_{A,E}$ (Interaction factor)	2.88	3.22	3.13
μ_{mp} (DhA mobile phase mobility) (x10^{-9}m^2/V·s)	-22.3	-25.0	-25.8

the case of this work) as determined by the capillary electrophoresis experiments. A μ_{sp} value of 39.94x10^{-9}m^2/V·s for pDADMAC was taken from literature (*40*).

In order to determine the two unknown parameters; $K'_{A,E}$ and μ_{mp}, the 'solver function' of Microsoft Excel 2000 was used. The "solver function" is a nonlinear regression method that minimises the least squares by simultaneous substitution of the unknown and known parameters of any given equation. In this case each different set of known parameters from Equation 12 for each of the 35 injections was used simultaneously to determine the unknown parameters of Equation 12 ($K'_{A,E}$ and μ_{mp}). A schematic of these two unknown parameters is shown in Figure 6.

RESULTS AND DISCUSSION

Plotting the mobility (μ_A) of the DhA$^-$ at various pH values over a range of pDADMAC concentrations the slopes of these curves decrease as the pH decreases. This is consistent with the decreasing ionicity of the DhA as the pH of the eluent decreases towards, and or past, the pK_a of DhA (6.77(*45*)). It is a result of this that no data has yet been obtained for pH 4.75, though it is believed that with larger capillary inter diameters (ID) it might be possible to observe the elution of DhA/DhA$^-$ aggregates. Assuming that the larger ID capillaries would allow for the elution of the DhA further calculations would be required in order to satisfy Equation 10 (i.e. x and y).

Figure 7 would suggest that DhA$^-$ is more easily retained by pDADMAC as pH increases, because the slopes of the plotted lines is greater at higher pHs.

In substituting all of the quantities that are known in regards to these separations into Equation 12 and solving for $K'_{A,E}$ and μ_{mp} we obtain the results shown in Table 3.

The data in Table 3 gives a quantifiable interpretation to the trends observed in Figure 7. The mobile phase mobility (μ_{mp}) of the DhA$^-$ increases, with pH, as the ionicity of the DhA$^-$ increases. The interaction factor $K'_{A,E}$, between DhA$^-$ and pDADMAC, reaches a maximum at pH 8.06.

Future work would need to include μ_{sp} values for each analyte at each pH, as the charged nature of some p-SPs is likely to change with pH. (*52*)

CONCLUSIONS

This electrokinetic chromatography method of determining the interaction factor between deprotonated dehydroabietic acid and poly-dimethyldiallyl-ammonium chloride at pHs 6.85, 8.06 and 10.93 is effective and simple.

The results of this work would suggest that deprotonated dehydroabietic acid is more easily retained by poly-dimethyldiallyl-ammonium chloride at pH 8.06.

Challenges in regards to eluent pHs below analytes' pK_a, as well as non-ultraviolet absorbing analytes, need to be met before this technique brings greater value and usefulness to the pulp and paper community.

ACKNOWLEDGEMENTS

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